

APPLICATION FOR PATENT

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TITLE: **PROCESS OF PRODUCING HEAT EXPANDABLE COMPOSITIONS AND FLEXIBLE ARTICLES CONTAINING SAME**

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SPECIFICATION

Field of the Invention

The invention relates to a process for producing a composition which, when subjected to heat, expands to form heat-insulating barriers. In addition, the invention relates to a process of producing flexible articles containing such compositions. The process consists of mixing into a resinous emulsion at room temperature a fire retardant until homogeneity is obtained; admixing into the resulting composition expandable graphite and extruding the resultant homogenous paste at room temperature onto a substrate. The product is then dried. The resulting product has particular applicability as a fire stop seal for door frame assemblies.

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Background of the Invention

Fire retardant, fire proofing, and even fire stopping materials and their method of production and use have been disclosed in the prior art. For example, European Patent 0 256 967 B1 discloses a process for the production of moldings by extrusion or injection molding of a mixture that contains polyvinyl chloride and a mixture of polyhydric alcohol at elevated temperature. Similar type processing is disclosed in European Patent 0 302 987 B1. Processing at such temperatures using thermoplastic mixtures presents processing difficulties.

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Likewise, the use of elevated temperatures are disclosed in U.S. Patent No. 5,094,780. The '780 patent is directed to the use of expandable graphite in fire retardant

intumescent moldings. The composition is heated in a mold at temperatures between 150°C. and 350°C. More suitable means for producing fire retardant materials are desired.

Summary of the Invention

The process of the invention comprises the steps of first dispersing into a resinous emulsion a fire retardant until homogeneity is obtained. Expandable graphite is then mixed into the resulting product until a homogeneous paste results. Both of these steps occur at room temperature. The resulting composition is then extruded at room temperature. The composition may be extruded onto a substrate. The substrate comprises either polyurethane, wax paper, polyester, polyethylene film, polypropylene film or mineral wool. In another embodiment, the substrate is composed of cementitious material. The resulting product is then dried.

The weight percent of expandable graphite in the composition just prior to extrusion is between about 5 to about 95 per cent. The amount of fire retardant in the composition just prior to extrusion is between 1 to about 70% by weight. The amount by weight of resinous emulsion in the composition prior to extrusion is between from about 25 to about 90 per cent.

The process of the invention offers considerable advances over the prior art since it is conducted at room temperature. Even the extrusion step may be conducted at room temperature.

When subjected to heat, the resulting article expands to form a heat-insulating barrier. In a preferred embodiment, the resulting article are molding strips which have particular applicability as fire-retardant barriers in doorways and pipes. In addition, the molding strips of the invention may be used to enclose pipes or other points of vulnerability in order to aid in the prevention of penetration of fire and/or smoke by intumescing and sealing off available pathways.

Detailed Description of Preferred Embodiments

The invention is directed to a process for producing heat insulating barriers. In the first step of the process a fire retardant is dispersed into a resinous emulsion. The composition is mixed until the fire retardant is homogeneous throughout the resinous emulsion. The mixing of fire retardant into resinous emulsion is conducted at room temperature.

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Examples of emulsions for use in the process of the invention are acrylic emulsions, polyvinyl acetate emulsions, silicone emulsions, and styrene butadiene emulsions. In one embodiment of the invention, a resinous aqueous emulsion of a polyvinyl acetate may be used. In addition to aqueous emulsions, the resinous emulsion for use in the composition of the invention may consist of emulsions of polymers within an organic solvent, such as hydrocarbons, like xylene and toluene. In addition, keto alcohols or similar co-solvents can be used. In a preferred embodiment, diacetone alcohol co-solvent is used in combination with water. In such instances, between about 0.5 to about 10 weight percent, preferably less than one weight percent of the resulting composition.

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The composition of the invention (prior to extrusion) contains between about 15 to about 90, preferably between about 25 to 90, most preferably between about 30 to about 60, weight percent of resinous emulsion.

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Suitable styrene-butadiene polymers may be characterized as those polymers having from about 99 to about 65, preferably 99 to 80, weight percent of a C₈-C₁₂ vinyl or vinylidene aromatic monomer and the remainder being butadiene. The styrenic moiety can be optionally substituted with a C₁-C₄ alkyl or hydroxy alkyl radical or a chlorine or bromine atom.

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Such polymers may further comprise one or more copolymerizable monomers containing a functional group. When present, the functional monomers are present in an amount from about 0.5 to about 6 weight percent. The functional monomers may be selected from the group consisting of (1) one or more C₃-C₆ ethylenically unsaturated carboxylic acids; (2) one or more amides of C₃-C₆ ethylenically unsaturated carboxylic acids, which amide may be substituted or unsubstituted at the nitrogen atom by a C₁-C₄ alkyl or hydroxy

alkyl radical; (3) one or more C₃-C₆ ethylenically unsaturated aldehydes; and (4) one or more C₁-C₆ alkyl or hydroxy alkyl esters of C₃-C₆ ethylenically unsaturated carboxylic acids. Suitable C₈-C₁₂ vinyl aromatic monomers include styrene, alpha methyl styrene and chlorostyrene. Part of the aromatic monomer may be replaced by small amounts of an alkenyl nitrile such as acrylonitrile. Suitable conjugated diolefins include the aliphatic diolefins such as 1,3-butadiene, isoprene and their chlorinated homologues. Up to about half, preferably less than about 20 percent of the conjugated diolefin may be replaced with an ester of acrylic or methacrylic acid; or a vinyl ester of a saturated carboxylic acid. Suitable esters are those of acrylic or methacrylic acid such as methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, hydroxyethyl acrylate, hydroxy ethyl methacrylate and the higher branched esters such as ethyl hexyl acrylate and ethyl hexyl methacrylate. Suitable vinyl esters include vinyl acetate.

The resin within the emulsion of the composition of the invention may further include commercially available acrylic resins such as those derived from acrylic acid, methacrylic acid, itaconic acid, fumaric acid, methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, butyl acrylate, ethyl hexyl methacrylate, ethyl hexyl acrylate, acrylamide, methacrylamide, N-methylol acrylamide, N-methylol methacrylamide and/or acrolein.

The acrylate type polymers may further be characterized as polymers consisting of from about 60 to 99.5, preferably from about 85 to about 94.5 weight percent of a C₁-C₈ alkyl or hydroxy alkyl ester of acrylic and methacrylic acid; from about 10 to 40, preferably from about 5 to 15 weight percent of one or more monomers selected from the group consisting of C₈-C₁₂ vinyl or vinylidene aromatic monomers, which may be unsubstituted or substituted by a C₁-C₄ alkyl radical or a chlorine, or bromine atom, and a C₃-C₆ alkenyl nitriles and acrylic and methacrylic acid. The acrylate polymers may optionally further contain from about 0.5 to 10, preferably less than 5 weight percent, of a functional monomer other than a C₁₋₈ alkyl or hydroxy alkyl ester of acrylic or methacrylic acid. Suitable monomers were discussed above in relation to the styrene-butadiene type polymers.

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The resin of the emulsion may further be an C₁-C₈ monoolefin-vinyl ester copolymer wherein the vinyl ester is an ethylenically unsaturated ester of a saturated carboxylic acid. Particularly preferred is vinyl acetate. Such copolymers typically comprise up to about 95 percent by weight of, preferably from about 5 to about 40 weight percent of a C₁₋₈ monoolefin. A C₂-C₃ monoolefin is preferred. The copolymer may further be derived from a hydroxy alkenyl ester of a C₁₋₈ saturated carboxylic acid. Lastly, the copolymer may optionally contain from about 0.5 to 10, preferably from about 0.5 to 5, weight percent of one or more of the functional monomers referenced above.

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The emulsion for use in the invention may further comprise a silicone emulsion. Such emulsions are well known in the art. See, for example, U.S. Patent No. 2,891,920; 3,294,725; 3,360,491; 2,702,276; 2,755,194; 4,194,988; 3,795,538, all of which are herein incorporated by reference.

The weight ratio of polymer:solvent in the emulsion is generally between 30:70 to about 70:30.

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In a preferred embodiment, the resinous emulsion is characterized as having a glass transition temperature, T_g, below -40°C. In those instances, where the glass transition temperature of the emulsion is not below -40°C., a liquid plasticizer may be used. Suitable plasticizers for decreasing the glass transition temperature of the emulsion to an acceptable level are octyl epoxy soyate, epoxy tallates, epoxidized soybean oil, epoxidized linseed oil, triphenyl phosphate, neopentyl glycol dibenzoate, glycerine, vegetable oil and mineral oil. Typically, no more than 1 to about 10 weight percent of plasticizer, based on the weight of the resin, is needed.

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Typically, the amount of resinous emulsion in the composition of the invention, prior to extrusion, is between from about 25 to about 90, preferably between from about 30 to 65, weight percent.

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Suitable for use as the fire retardant for use in the invention are conventional agents known in the art. Such agents include, but are not limited to, organic phosphates including an amine phosphate, a trialkyl phosphates such as tributyl phosphate and triethyl phosphate, halogenated alkyl phosphates such as tris (2,3-dibromopropyl) phosphate,

ammonium phosphates including diammonium phosphate and ammonium polyphosphates, melamine phosphate, melamine ammonium polyphosphate, diammonium sulfate and blends thereof, such as a blend of monoammonium phosphate and diammonium phosphate having a nitrogen-to-phosphorus ratio of at least about 1.25 and a blend of monoammonium phosphate, diammonium sulfate and diammonium phosphate having a nitrogen-to-phosphorus ratio of at least 1.25.

Preferred flame retardants for use in the invention include amine/phosphorus containing salts. In general, these are amine salts of phosphoric acid or lower alkyl esters thereof. Lower alkyl esters means that C₁-C₈ alkyl ester has been made of one or more sites on the phosphoric acid group. Most preferably, a C₁-C₄ alkyl esters are used and most preferably an ethyl ester or no ester group is used.

The amount of flame retardant in the composition (prior to extrusion) is between from about 1 to about 70, preferably between from about 10 to about 40, weight percent.

Further preferred as flame retardants are lower alkyl diamine phosphates, such as C₂-C₈ alkyl diamine phosphates, most preferably C₂-C₄ alkyl diamine phosphates. Due to its relatively high phosphorus content and since it can be obtained inexpensively from commercial sources, ethylene diamine phosphate is especially preferred.

Along with a fire retardant, a defoaming agent, surfactant and/or intumescent inorganic filler may also be dispersed into the resinous emulsion at the same as the fire retardant or before or after the introduction of the fire retardant. In any event, the defoaming agent, surfactant and/or intumescent inorganic filler is added to the resinous emulsion prior to the addition of the expandable graphite.

In a preferred embodiment, a non-silicone defoamer is used. In a preferred embodiment of the invention, an oil-based defoamer comprising a plurality of petroleum hydrocarbons and fatty amides is used. Such defoamers include the fatty amides such as the reaction products of a (i) polyamine such as ethylene diamine, butylene diamine, diethylene triamine, triethylene tetramine, hexamethylene diamine, decamethylene diamine, hydroxyethyl ethylene diamine, and 1,3-diamine-2-propanol, and (ii) fatty acid such as those having from 6 to 18 carbon atoms.

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Intumescant expandable inorganic fillers which have been found to render particularly advantageous results include perlite, vermiculite, expandable glasses, micas, clay, talc, borosilicates, cokes, charcoals, hard coals, brown coals, graphite granules, cork granules, wood granules, calcium carbonate, cereal grains, cork, bark granules, expandable clay, foamed concrete, metal sponge, pumice, tuff and/or lava. In a preferred embodiment, a hydrated aluminum silicate is used, such as those commercially available which contain mostly kaolin with a relatively small amount of titanium oxide. When present, such inorganic fillers may be present in the composition, prior to extrusion, in an amount between from about 1 to about 50, preferably between from about 1 to about 25, weight percent.

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As the surfactant, either anionic, cationic or non-ionic surfactants may be used. Exemplary non-ionic surfactants are fatty acid alkanolamides, linoleamide, tallow monoethanolamide ethoxylate, ethylene oxide adducts of a higher primary alcohol such as a nonylphenol, such as Surfonic N-85, or an ethoxylated amine as well as sorbitan monooleate, polyoxyethylene (2) oleyl ether, polyoxyethylene (20) sorbitan monooleate, a C₆-C₁₁ linear alcohol ethoxylate as well as a block copolymer of propylene and ethylene oxide, glycetyl laurate. In a preferred embodiment of the present invention, a surfactant comprising octylphenoxy polyethoxyethanol, water, and polyethylene glycol was used. The composition of the invention, prior to extrusion, may further comprise between from about 1 to about 25 weight percent of surfactant.

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Usual optional adjuvants can also be mixed with the fire retardant into the resinous emulsion. These adjuvants include reinforcing agents, process aids, stabilizers, pigments, coupling agents or a biocide. In a preferred embodiment of the invention, the composition contains less than one weight percent of a biocide such as commercially available biocides containing glycol ether and 3-iodo-2-propynyl butyl carbamate. In addition, reinforcing agents, principally fibrous substances such as polyesters, may be added with the fire retardant into the emulsion. Typically, the composition (prior to extrusion) contains no more than 5, generally less than 1, weight percent of such components.

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In the second step of the invention, an expandable graphite is admixed, preferably at room temperature, with the emulsion containing dispersed fire retardant and, optional,

defoamer, inorganic filler and/or surfactant. Expandable graphites for use in the present invention are graphites of any type which are expandable on heating. They may be solid, swollen or already partly expanded and may expand, for example, by 10 to 800 percent by volume or more. Such expandable graphites are well known in the art. They are in general graphites in whose interstitial planes foreign atoms, ions or molecular groups are incorporated.

Preferred graphites are so-called NO_x and SO_x expandable graphites which can be prepared by the action of sulfuric or nitric acid on graphite, optionally in the presence of an oxidizing agent, such as hydrogen peroxide). The acid components of the resulting product are generally encapsulated within the graphite matrix. Suitable expandable graphites can also optionally be obtained by an electrochemical method. The composition of the invention, prior to extrusion, contains between from about 5 to about 95, preferably from about 10 to about 40, weight percent of expandable graphite.

A particularly desirable composition of the invention is one which contains the following components:

Ingredient	Approximate weight percentage range
Resinous Emulsion	30-60
Expandable graphite	10-40
Fire retardant	10-40
Surfactant	<5
Remainder filler materials	Balance

Once this mixture has been thoroughly mixed and blended, preferably in the mixing tank, the mixture is preferably extruded to create strips of a desired thickness, width, and length. The mixture may be extruded onto a thin flexible substrate. Such substrates may be composed of wax paper, polyester, polyurethane, mineral wool, polyethylene film, polypropylene film or may even be a cementitious substrate. In the preferred method of production, the extrusion process is performed with a ram extruder and the extrusion occurs at ambient or room temperature.

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Once extruded, the strips are allowed to dry. Drying of the strips may occur at room temperature. Alternatively, drying of the strips may be performed through the addition of a drying agent such as Portland cement to the mixture (prior to extrusion), by chemical means (such as by the addition of crosslinking agents to the mixture prior to extrusion) or by physical means, such as by microwave radiation.

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The composition of the invention expands upon an exposure to heat, thereby creating a seal in the spread of fire and/or smoke. The composition consists of a resinous emulsion into which is admixed an expandable graphite and a fire retardant agent. In an alternative embodiment, an inorganic intumescent filler may be used in conjunction with the fire retarding agent.

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When applied, the flexible intumescent device of the present invention remains dormant until the heat of a fire activates the flexible intumescent device. When activated by the heat of a fire, the flexible substrate will intumesce or similarly expand to close the gaps, cavities, or channels normally existing between each door and its respective frame in the closed position. By applying the flexible intumescent device to the outermost perimeter of each door in the preferred embodiment, the fire activated flexible intumescent device will seal off the gap between each door and frame, effectively preventing the progression of the fire.

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The composition produced by the process of the invention may further be easily applied by encasing the circumference of a pipe or similar conduit. The expansion of the flexible intumescent device will distance the effects of the fire and maintain the soundness of the pipe or similar conduit.

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The following examples will illustrate the practice of the present invention in its preferred embodiments. Other embodiments within the scope of the claims herein will be apparent to one skilled in the art from consideration of the specification and practice of the invention as disclosed herein. It is intended that the specification, together with the examples, be considered exemplary only, with the scope and spirit of the invention being indicated by the claims which follow.

EXAMPLES

Example 1. To a polyvinyl acetate emulsion, was added octylphenoxypolyethoxyethanol and Colloid 796, a defoamer of Rhone-Poulenc. These ingredients were mixed at room temperature until homogeneous. To the resulting mixture was slowly added, while stirring, 2-amino-2-methyl-1-propanol, kaolin, ethylene diamine acid phosphate, carbon black and polyethylene terephthalate. After each of the ingredients was added the resulting mixture was stirred until homogeneous. Expandable graphite was added until a homogeneous paste was obtained. Each of the components was added as specified above at room temperature.

The resulting mixture was extruded at room temperature onto a flexible Mylar polyethylene terephthalate film. To the top surface was also applied a thin flexible protective sheath, such as a plastic strip. The article is allowed to dry at room temperature. Flexible intumescent strips were then cut to the desired size.

Prior to extrusion, the composition contained about 51% of polyvinyl acetate emulsion, 0.5% octylphenoxypolyethoxyethanol, 0.4% 2-amino-2-methyl-1-propanol, 0.3% Colloid 796, 16% ethylene diamine acid phosphate, 7.5% kaolin, 22.3% expandable graphite, 0.9% polyethylene terephthalate, and 0.02% carbon black. All percentages expressed herein are weight percentages.

Example 2. To 400 g of an emulsion of copolymer comprising 71 weight percent of methyl methacrylate and 29 weight percent styrene is added 30 grams of Surfonic N-85 and 20 g of Colloid 796. These ingredients are mixed at room temperature until homogeneous. To the resulting mixture is slowly added, while stirring, 80 grams of calcium carbonate, 150 g of cementitious drying aid and 120 g of triethylphosphate. After the addition of each of these ingredients, the resulting mixture is stirred. 200 g of expandable graphite is then added until a homogeneous paste is obtained. Each of the components are added at room temperature. The resulting mixture is extruded at room temperature onto a table. To the top surface is applied a thin flexible protective sheath, such as a plastic strip. The article is

allowed to dry at room temperature. The flexible protective sheath is removed after drying. Flexible intumescent strips are then cut to the desired size.

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Example 3. To 500 g of polysilicone emulsion is added 30 g of polyoxyethylene (20) sorbitan monooleate, and 20 g of Colloid 796. These ingredients are mixed at room temperature until homogeneous. To the resulting mixture is slowly added, while stirring, 200 g of vermiculate and 120 g of diammonium phosphate. After the addition of each of these ingredients, the resulting mixture is stirred. 130 g of expandable graphite is then added until a homogeneous paste is obtained. Each of the components are added at room temperature. The resulting mixture is extruded at room temperature onto a thin layer of polypropylene film. The article is allowed to dry at room temperature. Flexible intumescent strips are then cut to the desired size.

From the foregoing, it will be observed that numerous variations and modifications may be effected without departing from the true spirit and scope of the novel concepts of the invention.